Adsorption Of Methyl Violet From Aqueous Solution Onto Modified Ampo

Yuliani. HR[1]
1] Jurusan Teknik Kimia, Politeknik Negeri Ujung Pandang,
Jl. Urip Sumoharjo KM.10 Tamalanrea Makassar 90112 [Sul-Sel]
Email : yulihr07@yahoo.com

Abstract

This paper presents our contribution to remove of methyl violet from aqueous solution by adsorption. The adsorbent used is ampo from Wadas Lintang, Wonosobo, Center of Java Indonesia. This ampo has been modified by several treatments such as iron pillaring and pillared followed by calcination at 400 ^{o}C. The adsorbent are used to fix methyl violet from aqueous solution at pH = 7. The maximum of adsorption differs according to the treatment. The concentration of methyl violet from aqueous solution has been measured by batch techniques and with UV-Vis analysis adsorption. The experimental data were correlated reasonably well by Langmuir isotherm and the isotherm parameters qmax and b have been calculated. The adsorption capacities were found to be 187.04 and 62.20 mg of methyl violet per g of adsorbent for modified ampo and natural ampo.

Keywords: *Methyl violet, Ampo, adsorption capacity, modified ampo*

Introduction

Color is an effluent characteris which is easily detected and easily compared to its source. Some dyes are stable to biological degradation, toxic and damage to the aesthetic naturare of the enviromenment. One of colors that is often used in textile industry is methyl violet (mv). Methyl violet is faction of basic dye obtained from oxidation of nitrogen. This dye applied at textile industry for wool fiber quenching, silk, nylon, acrylate and modakrilat, besides also applied at craft industry. Methyl violet dangerous for health because can cause mutation and cancer at man and very dangerous for animal (Fairus, S, dkk, 2009).

This dye before exhaust into water is done decolorize applied some methods include coagulation, electrocoagulation, flotation, chemical oxidation, filtration, ion-exchange, membrane separation, aerobic and anaerobic microbial degradation (Ozacar and sengil, 2004). All of these methods suffer from one or another limitations, and none of them were succefully removing the color from waste water.

Adsorption currently appears to offer the best method for overall treatment and it can be expected to be useful for a wide range of compounds, more so than any of the other listed processes. This method is easily done and cheap at process. Adsorption process there are two factor is having an effect on there are adsorbent and adsorbate. Adsorbents often applied are activated carbon, coal, fly ash, wood, silica, shale oil ash, fuller's earth, zeolite, perlite, clay materials and agricultural waters. Activated carbon widely used adsorben but quite expensive, higher the quality and greaster cost. This has led many workers to research for cheaper adsorben. Ampo is a mineral not soluble in water in its natural form. Ampo's ability in adsorbing bitter taste in papaya leaves indicates that

Ampo has adequate surface area so it can be concluded that a potential ampo adsorbent. Usage of ampo directly as adsorbent has constraint that is when it in the water will be brittle and swell as a result not optimal adsorption ability. To increase the adsorption capacity and characteristics is performed by ampo modification with pillarisation method. Pillarisation is an intercalation pillaring agent into ampo interlayer. Synthesis of pillared ampo includes making of suspension, pillaring agent with a solution $FeCl_3.6H_2O$ hydrolyze with NaOH 0.2 M 0.2 M on the ratio of OH / Fe 2 the next step is intercalation of pillaring agent into ampo suspension with Fe/ampo ratio 2. After intercalation, process continue with washing and calcination at apply temperature 400^{o}C and application adsorption methyl violet and characterization include surface are, scanning electronic microscope and basal spacing.

FUNDAMENTAL

a. Methyl violet

Methyl violet is group of basic dye with chemistry formula $C_{25}H_{30}N_3Cl$ and molecule weight 408 g/mol. Chromophore from methyl violet and methylene blue have the cation so that this dye grouped in group of basic dye (Ozacor and Sengil, 2006). Methyl violet dangerous for health because can cause mutation and cancer at man and very dangerous for animal (Fairus dkk, 2009). Struktur of metyl violet can been at figure 1.

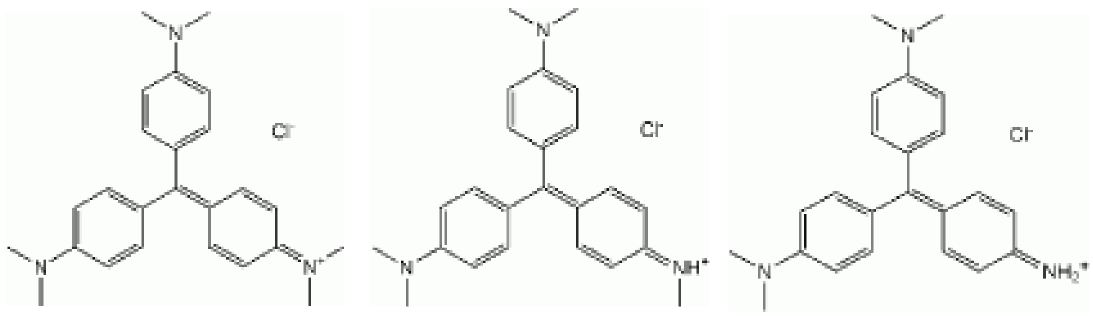

Figure 1. The chemical structure of methyl violet

b. Ampo

Ampo is natural material located st laying between soil layer and measures up to unique that is firm like stone in the situation dry and its the hardness will lose when staying in water. Ampo there is in some districts in Indonesia that is Wonogiri, Wonosobo, Yogyakarta, Tegal, Pemalang Brebes, Tuban, Bali and Lombok island. The name of ampo differs in every place, in Central Java, East Java and Bali calls it ampo, in West Nusa Tenggara Lombok island especially tribe Sasak calls it katen land. Ampo by public exploited as camilan, hot drug and prevents pruritis and applied as adsorbing bitter taste at papaw leaf (Yoesfile, 2007). Public in hamlet Bektiharjo, vollage Semanding, sub-province Tuban - East Java consumes ampo as light snacks. The taste is crispy and believed can eliminate pain in bone taste in whole part of body (Utomo, 2009). Based on analysis difraction of X-ray compiler clay mineral ampo Wonosobo that is quartz,calcium carbonat, nontronite, magnesium chlorite hidrokside and montmorillonit (yuliani, 2009). Image of ampo can be seen on figure 2.

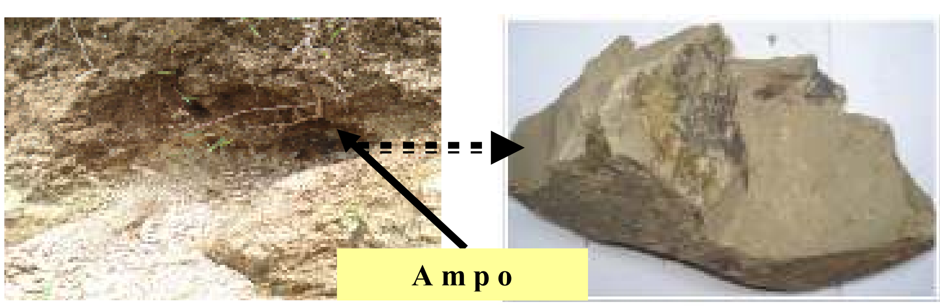

Figure 2. Location Ampo and Ampo

c. Pilarisation

Pilarisation is interkalation of agent pemilar into laminated material structure then is continued calcination. Interkalation is an insertion process of atoms or molecules into between layers laminated material without destroying the layer structure (Arfaoui dkk., 2007). Atoms or molecules which will be inserted called as intercalate while layer which is place of intercalate called as intercalant, with the entry of intercalate into intercalant hence formation owned by intercalant to experience change. This change happened because layer closest hindered by intercalat having molecule measure bigger than the origin molecule. Pillared clay process presented at figure 3.

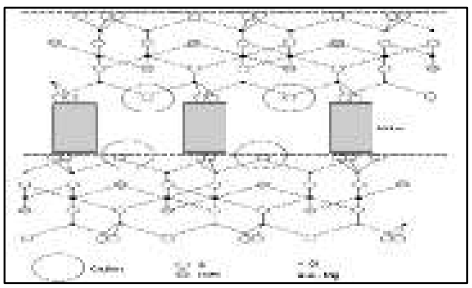

Figure 4. Pillar process (Yang, 2003)

d. Adsorption

Adsorption is one of technology applied in separation process, as does with imbibition process method, distilation, and extraction. Adsorption is processing adsorption of solute from fluid to solid active surface, this phenomen happened because there is uneven styles at boundary intersurface. Adsorption process consisted of three steps that are (1) adsorbate molecular difusion to surface adsorbent, (2) transfer of adsorbate into pore adsorbent and (3) forming of monolayer adsorbate. Adsorption process illustrated at figure 4.

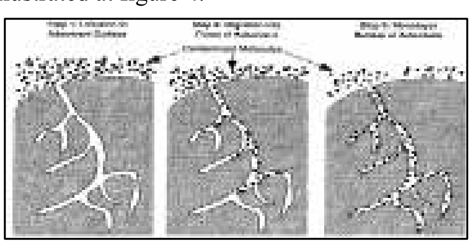

Figure 4. Adsorption process at adsorbent (www.fineprint.com)

Adsorption isotherm can be used to predict the design of single batch and langmuer method can be calculated adsorption capacity adsorption. A schematic diagram is shown in figure 5.

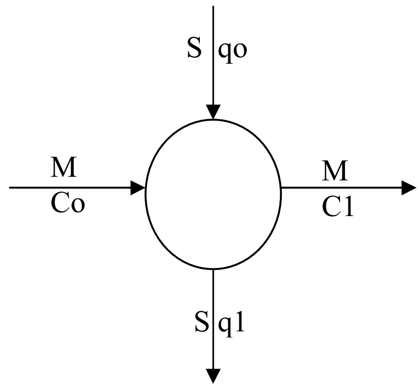

Figure 5. Single batch adsorption

Where the effleunt contain M l water and an initial concentration Co, which is to be reduce to C1 in adsorption process. In the trearment stage S g ampo and modified ampo is added and the methyl violet concentration on the solid chane from qo=0 to cq1.

Material balance singlde batch :

$$\mathrm{Co.\,M + qo.S = C1.M + q1.S} \quad \text{....................(1)}$$

$$\frac{\mathrm{S}}{\mathrm{M}} = qe = \frac{\mathrm{Co - C1}}{\mathrm{q1}} = .\frac{\mathrm{Co - C1}}{\mathrm{m}} xVa.........(2)$$

Adsorption maximum capacities is calculated based on model Isotherm Langmuir posed at equation (3). Equation of Langmuir told by Ozacor and sengil (2006).

$$q_e = \frac{q_m .b\, C_e}{1 + b.Ce} \quad \text{...............................(3)}$$

Equation (3) linear to become :

$$\frac{\mathrm{Ce}}{\mathrm{qe}} = \frac{1}{qm.b} + \frac{Ce}{qm} \text{..........................(4)}$$

MATERIAL AND METHOD

The natural ampo and modified ampo samples were obtained from Wadas Lintang, Wonosobo, Center Java with cation change capacity 31.80 meq/100 g. The chemical composition of ampo Wonosobo are SiO_2 49.2%, Al_2O_3 0.43%, CaO 1.95%, MgO 2.13%, Na_2O 0.45% dan H_2O 23.24%. This experiment consisted of pillaritation ampo and characterisation. This research consisted of process of pillared ampo and characteristic. Making of pillared ampo is preparation of research material (ampo and supporter material), pilarisation (making of suspension and pillared agent, interkalation, wash and calcination), adsorpsi metyl violet and karakterisation. Adsorpsi methyl violet is through adsorption methyl violet in water. Characterisation pillared ampo and natural ampo consisted of determination bassal spacing, surface area, size distribution pore, and structural morphology and determination of adsorption maximum capacities at adsorption methyl violet.

RESULT AND DISCUSSION

1. Adsorption Methyl Violet

Adsorption methyl violet aim to the application of pillared ampo and natural ampo as adsorbent by the way of determining adsorption capacities. Based on adsorption capacities value obtained, hence requirement of adsorbent theoretically knowable. Determination of adsorption capacities is done by doing test at variable representing to eight various concentration of methyl violet. Concentration of methyl violet tested that is 100 - 800 ppm. Data result of research in concentration at equilibrium measured through maximum absorbance. Absorbance obtained is converted to become concentration with ploting data result of measurement at standard curve or through equation which has been made at standard curve. Concentration of equilibrium (Ce) and adsorption capacities in the situation balance (qe) calculated applies equation (3). Value Ce and qe is connected, that is formed adsorption curve methyl violet in water like illustrated at figure 5.

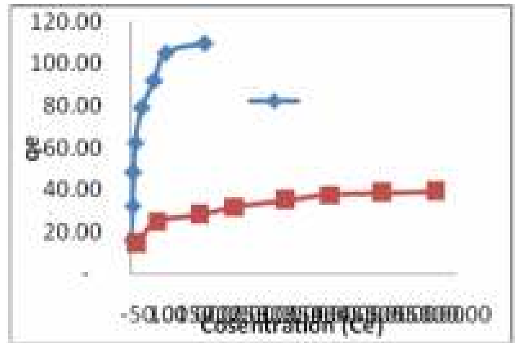

Figure 5. Equilibrium adsorption methyl violet in water

Figure 5 indicates that either ampo without pillar and also ampo is pillar at calcination temperature 400 ^{o}C has ability of adsorption methyl violet in high water for low kosentrasi, but ability of the adsorption starts declines at kosentrasi 600-800 ppm. illustration of Adsorption presented by the picture follows isotherm adorpsi type I is processing the adsorption forms layer monolayer and expressed with equation of Freundlich and Langmuir. Calculation of adsorption maximum capacities applies Langmuir method is done by the way of its the equation linear according to at equation (3). Adsorption capacities is obtained by finally the equation in linear regression. Result of calculation in presenting at Tabel 1.

Tabel 1. Adsorption capacities methyl violet in water

No	Fe/Ampo [mmol/g]	b [l/mg]	Adsorption capacities 'qmax' [mg/g]
1	0	0.0237	41.5023
3	2	0.1093	117.1008

Tables 1 indicates that pillared ampo has adsorption capacities of adsorption maximum methyl violet in water bigger than natural ampo. Improvement of adsorption capacities at pillared ampo is caused existence of improvement of surface area and bassal spacing, in detail will be studied at the subject of characterisation.

2. Characterisation

Characterisation of natural ampo and pillared ampo aim to know surface area, size distribution pore, bassal spacing and image of surface structure morfologi. Success of pilarisation influenced by some factors that is degree of hydrolysis (OH/FE , comparison (metal/clay , cosentrasi of metal ion, temperature and pilarisation time, temperature and calcination time (Canizares dkk., 1999, Cho and Ko, 2000, Sychev dkk., 2000).

Bassal spacing

Pillared ampo with iron oxide (Fe_2O_3) based on interkalation of pillared agent which in the form of cation complex of iron metal into interlayer silicate ampo. Chemistry process involving in interkalation is cation exchange. Intercalation ampo applies polihidroksi cation of iron aim to replace cations found on interlayer silicate montmorilonite and nontronite in ampo. After interlacation continue calcination so that is formed iron metal oxide pillars [Fe_2O_3] what dissociates and pillar interlayer silicate in ampo. Ampo which has been pillar Characterisation of bassal spacing that be knowable level of friction of distance between layers ampo. If already happened pillar hence will seen existence of friction of distance between layers ampo marked with change of bassal spacing. Change of this knowable basal spacing passed friction of 2θ . Height of pillar formed is determinable with calculating difference between bassal spacing ampo is pillared Fe_2O_3 with thickness of silicate layer 96 ^{o}A (Cheng dkk., 1994, Hutson dkk., 1999). Bassal spacing from pillared ampo Fe_2O_3 and natural ampo is analysed by X-ray diffractometer. Result of analysis is illustration in figure 6.

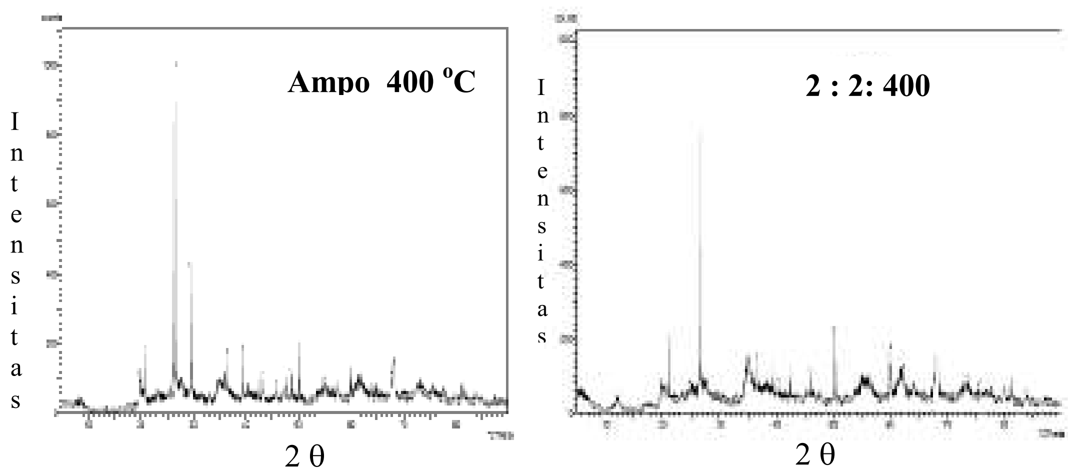

Figure 6. Difragtogram ampo dan pillared ampo at 400 ^{o}C

Figure 6 indicating that ampo is calcination at 400 ^{o}C happened collapse at structure interlayer silicate is marked with loss of 2θ = 5814^o for mineral montmorillonite and nontronite which is highest basal spacing at ampo. Pillared ampo 2 : 2 : 400 ^{o}C experiences friction of value 2θ to become 56^o with bassal spacing 15.76875 ^{o}A and 10,05129 ^{o}A for natural ampo. This thing indicates that with pilarisation can increase bassal spacing which is one of indicator success of pilarisation besides pilarisation also can take care of stability to temperature. Change of this basal spacing indicates that already happened intercalation of pillared agent into between silicate layers at ampo and after calcination is formed ferrous oxidation pillar (Fe_2O_3) as pillar between layer of ampo.

Surface area and size distribution pore

Physical character applied to indication characteristic of pillared ampo with iron oxide is surface are, porosity and stability thermal.it's primary factor of pillared clay to show worked as adsorbent (Vansant, 1998; Fatimah, 2006). Adsorption Gas analytical method is method which applicable to determine specific surface area from ampo. The other information through this analysis for example size distribution pore and adsorption isotherm from sample. Surface area is obtained based on determination of capacities monolayer showing the many molecules which can be adsorption at surface of solid material. Surface area is calculated to applies method Bruaner-Emmet-Teller (BET) from data adsorpsi-desorpsi N_2, Po = 747.55 mmHg and temperature 77.35 K applies gas sorption analyzer (Nova 2000). At research of pilarisation pillared ampo by Fe_2O_3 2: 2: 400 ^oC can increase surface area out of 33.027 m2/g becomes 99.5618 m2/g. Improvement of surface area pillared ampo caused existence of Fe_2O_3 is acting as pillar interlayer ampo besides the happening of damage at natural ampo.

Pore of ampo assume is the slit form then in calculation size distribution pore based on data adsorpsi-desorpsi gas isotherm N_2 used de Boer method. This method based on thickness of adsorbate patching at pore wall. Size distribution pore illustrated at figure 7. pilarisation generates the forming of new pore. Forming of new pore as result of pilarisation happened also at research done by Hutson dkk (1999) about pilarisation clay applies pillar material Al_2O_3.

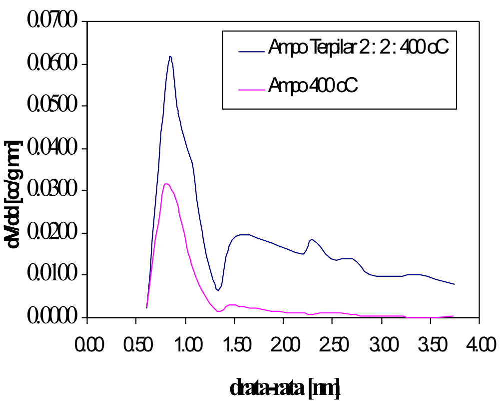

Figure 8. Size distribution pore ampo and modified ampo

Structural Morphology

Surface analysis ampo without pillar and pillared ampo Fe_2O_3 is used scanning electro microscope (SEM) presented in figure 8. Ampo without pillar shows surface morphology is the form of like shiver, while at ampo is pillar seen white block. Pilarisation ampo has a number of spaces between layers at the surface causing surface of pillared ampo becomes more porous compared to natural ampo. Space between this pillars can have the character of micro and or mesopori. Smallest distance between the layers can influence arrangement of space filler molecules between layers (Bergaya,etc., 1995; Negara, 2005).

CONCLUSIONS

1. Ampo is pillar Fe_2O_3 can be through interkalation of pillar agent into between layers montmorillonite and nontronite in ampo.
2. The adsorption capacities were found to be 187.04 and 62.20 mg of methyl violet per g of adsorbent for modified (pillared) ampo and natural ampo.
3. Pilarisation ampo applies polihidroksi cation of iron with comparison of Fe/ampo 2 and ratio OH/Fe 2 can increase character physical of like bassal spacing, surface area specifik and adsorption capacities methyl violet .

REFERENCES

Arfaoui, S., Frini-Srasra, N., and Srasra, E., 2007, Modelling of The Adsorption of The Chromium Ion by Modified Clays, Desalination 222, 474-481.

Canizares, P., Valverde, J.L., Kou, M.R.S and Molina, C.B., 1999, Synthesis and Characterization of PILCS with Single and Mixed Oxide Pillars Prepared from Two Different Bentonites. A Comparative study, Microporous and Mesoporous (29) 267-281.

Chen, J.P., Cheng, L.S., Hauslade, M.C., Kikkinide, E.S., and Yang, R.T., 1994, Superior Catalysts for Selective Catalytic Reduction of Nitric Oxide, Pittsburg Energy Technology Center, U.S. Department of Energy, Buffalo, 1-18.

Do, D.D., 1998, Adsorption Analysis: Equilibria and Kinetics, Series on Chemical Engineering, Vol 2, Imperial College, 13 – 16.

Fairus, S., Suhartono, J., Nurhayati dan Ariefa, F., 2009, Study Adsorpsi Zat Warna Methyl Violet dengan Menggunakan Kulit Pisang, Prosing Seminar Teknik Kimia “Kejuangan”, UPN, Yogyakarta.

Fatimah, I dan Wijaya, K., 2006, Pengaruh Metode Preparasi Terhadap Karakter Fisikokimiawi Montrollonit Terhdap ZrO_2, Akta Kimindo, 1(2), 87-92.

Hutson, N.D., Hoekstra, M.J and Yang, R.T., 1999, Control of Microporosity of Al_2O_3-Pillared Clays : Effect of pH,

Calcination Temperature and Clay Cation Exchange Capacity, Microporous and Mesoporous Material 28, 447-459.
Long, R.Q., and Yang, R.T., 1999, Selective Catalytic Reduction of Nitrogen Oxide by Ammonia over Fe^{3+}-Exchanged TiO_2-Pillared Clay Catalysts.
Negara, S.I., 2005, Preparasi Krom Oksida-Montmorillonit dan Aplikasinya untuk sorpsi Benzena, Tesis S2 Ilmu Kimia, UGM, Yogyakarta.
Ozacar, M. and Sengil, I.A., 2006, A Two Stage Batch Adsorber Design for Methylene Blue removal to Minimize Contact Time, Environmental Management 80, 372-379.
Rightor, E.G.Tsou., Pinnavaia, M.T.J., 1991, Iron Oxide Pillared Clay With Large Gallery Height : Synthesis and Properties as a Fischer-Tropsch Catalyst, Journal of Catalyst, I, 130
Simpen, N.I, 2001, Preparasi dan karakterisasi lempung montmorilonit teraktivasi
Sychev, M., Shubina, T., Rozwadowski, M., Sommen, A.P.B., Beer, V.H.J.D and Santen, R.A.V., 2000, Characterization of microporosity of chromia-and titania-pillared montmorillonites differing in pillar density. I.Adsorption of Nitrogen, Microporous adnd Mesoporous Material, 37, 187-200.
Utomo, T.G., 2009, Ampo, Kuliner Masa lalu Bumi Ronggolawe, Duta Masyarakat, 4.
Yang, R.T, 2003, Adsorbents Fundamentals and Applications, John Wiley and Sons, USA.
Yoesfile, 2007, The Magic of Lempung (Ampo), www. WordPress.Com
Yuliani, 2009, Karakterisasi ampo dan aplikasi dalam menjerap methyl violet, Seminar Nasional Kimia Lingkungan UNAIR, Surabaya
------------. Adsorpsi, www.fineprint.com
------------. Methyl Violet, ww.wikipedia.com